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OPTICAL GLASS FILTER AND ULTRAVIOLET REGION TRANSMISSIVITY OR ABSORBANCE CALIBRATION METHOD THAT USES THE SAME

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Specification

1. Title of the invention

OPTICAL GLASS FILTER AND METHOD FOR CALIBRATING THE TRANSMISSIVITY OR ABSORBANCE WITHIN THE ULTRAVIOLET REGION

2. Patent Claims

1. An optical glass filter for calibrating the transmissivity or absorbance within the ultraviolet region characterized by the addition of 0.001 ~ 0.2 wt% of CeO_2 to a fluorophosphate glass which includes, in terms of wt%, 8 ~ 40% of P_2O_5, 5 ~ 35% of AlF_3, 30 ~ 75% of RF_2 (R is at least one type of metal selected from among Ba, Sr, Ca, Mg, & Zn), 0 ~ 40% of R'F (R' is at least one type selected from among Li, Na, & K), and 0 ~ 15% of $R''F_m$ (R" is at least one type of metal selected from among La, Y, Gd, Si, B, Zr, & Ta, whereas m is the atomic value of the metal R") and wherein no more than 7/10 of the aforementioned metal fluorides AlF_3, RF_2, R'F, and/or $R''F_m$ can, if necessary, be substituted with metal oxides.

2. A method for calibrating the transmissivity or absorbance within the ultraviolet region that uses the optical glass filter specified in Claim 1.

3. Detailed explanation of the invention

(Industrial application fields)

The present invention concerns an optical glass filter as well as a method for calibrating the transmissivity or absorbance within the ultraviolet region by using the same.

[1] Numbers in the margin indicate pagination in the foreign text.

(Prior art)

A concentration measurement based on the absorptiometric method makes use of the attribute that a substance bears a peculiar light absorption coefficient at a specified wavelength, according to which a substance is specified by using a wavelength gauge, and its concentration is measured by using a transmissivity or absorbance gauge.

Spectrophotometers based on the absorptiometric method are being used extensively not only as pollution gauging instruments for determining pollutant substances within waters or soils but also as medical drug analyzing machines or clinical analyzing machines, and it has become an important goal to secure the performances & reliabilities of these analyzing machines.

At present, ND (neutral density) glass filters, metal membrane filters, & potassium bichromate solution filters are being used for calibrations of the transmissivities or absorbances of /2 these spectrophotometers.

The aforementioned ND glass filters, however, include large quantities of coloring ions such as Fe, Co, etc. and therefore cannot transmit beams the wavelengths of which are shorter than 350 nm, due to which they are unusable for the calibration of the transmissivity or absorbance within the ultraviolet region.

Moreover, the reliabilities of measurement values yielded by metal membrane filters become adversely affected by stray beams derived from reflection beams used for the calibration of the transmissivity or absorbance within the ultraviolet region.

Potassium bichromate solution filters are also being used for the calibration of the transmissivity or absorbance within the ultraviolet region, although they are plagued with the shortcomings listed below.

(1): A solution filter can be used only once and therefore cannot be reused.

(2): The solution preparation is cumbersome, and the preparation technique requires skills.

(3): Conspicuous measurement value irregularities are incurred due to the solution preparation.

(4): High-purity reagents of the likes of potassium bichromate & perchloric acid are necessary.

(5): Such instruments as high-precision scales, chemical analysis instruments, etc. are necessary for preparing solutions.

(6): Since potassium bichromate is a designated pollutant substance, its effluent must be properly treated.

(Problems to be solved by the invention)

The objective of the present invention, which has been conceived for the purpose of eliminating the aforementioned filters of the prior art for calibrating the transmissivity or absorbance, is to provide an optical glass filter for calibrating the transmissivity or absorbance within the ultraviolet region which affords an excellent precision, handling friendliness, etc. and can also be used over a relatively broad wavelength range within a wavelength region shorter than 350 nm as well as a method for using the same.

(Mechanism for solving the problems)

The aforementioned objective of the present invention has been achieved by adding a specified quantitative ratio of CeO_2 to a fluorophosphate glass bearing the following specified composition.

In other words, the optical glass filter of the present invention for calibrating the transmissivity or absorbance within the ultraviolet region is characterized by the addition of 0.001 ~ 0.2 wt% of CeO_2 to a fluorophosphate glass which includes, in terms of wt%, 8 ~ 40% of P_2O_5, 5 ~ 35% of AlF_3, 30 ~ 75% of RF_2 (R is at least one type of metal selected from among Ba, Sr, Ca, Mg, & Zn), 0 ~ 40% of R'F (R' is at least one type selected from among Li, Na, & K), and 0 ~ 15% of $R''F_m$ (R'' is at least one type of metal selected from among La, Y, Gd, Si, B, Zr, & Ta, whereas m is

the atomic value of the metal R") and wherein no more than 7/10 of the aforementioned metal fluorides AlF_3, RF_2, R'F, and/or $R''F_m$ can, if necessary, be substituted with metal oxides.

In the following, the present invention will be explained in detail.

To begin with, the reasons for limiting the quantitative ratios of the respective components of the fluorophosphate glass forming the matrix material of the optical glass filter of the present invention will be explained below.

In a case where the ratio of P_2O_5 is lower than 8%, the glass becomes unstable, whereas in a case where the same exceeds 40%, the chemical endurance deteriorates, and therefore, the quantitative ratio of P_2O_2 is limited to 8 ~ 40%.

In a case where the ratio of AlF_3 is lower than 5%, the chemical endurance deteriorates, whereas in a case where the same exceeds 35%, the glass becomes unstable, and therefore, the quantitative ratio of AlF_3 is limited to 5 ~ 35%.

In a case where the ratio of RF_2 is lower than 30% or higher than 75%, it becomes impossible to obtain a sufficiently stable glass, and therefore, the quantitative ratio of RF_2 is limited to 30 ~ 75%.

In a case where the ratio of R'F exceeds 40%, not only does the chemical endurance deteriorate but the molten R'F also becomes excessively evaporated, and therefore, the quantitative ratio of R'F is limited to 0 ~ 40%.

In a case where the ratio of $R''F_m$ exceeds 15%, not only does the glass become unstable but the solubilization also becomes difficult, and therefore, the quantitative ratio of $R''F_m$ is limited to 0 ~ 15%.

It is also possible, furthermore, to substitute no more than 7/10 of the aforementioned metal fluorides AlF_3, RF_2, R'F, and/or $R''F_m$ with metal oxides.

The optical glass filter of the present invention for calibrating the transmissivity or absorbance uses, as a base, the fluorophosphate glass wherein the quantitative ratios of the respective components thereof are limited for the aforementioned reasons, and it is obtained by

adding, to this base, 0.001 ~ 0.2 wt% of CeO_2. In a case where CeO_2 exists as Ce^{3+} within the base glass, an absorption peak existing in the vicinity of 350 nm becomes surprisingly shifted to 300 nm or below in the case of an ordinary silicae glass, etc., and such a state comes to bear a moderate /3 transmissivity curve over a broad range of 200 ~ 300 nm, based on which it has become possible to calibrate the transmissivity or absorbance over a relatively broad wavelength range within a wavelength region shorter than 350 nm.

The aforementioned absorption pattern does not vary significantly even in cases the types & internalization ratios of divalent components within the fluorophosphate base glass comprising of the P_2O_5 & metal oxide satisfying the aforementioned compositional range are varied, and furthermore, similar results were obtained even in a case where the quantitative ratio of the divalent component was lowered and where the quantitative ratio of the monovalent component or trivalent component or a component with an even higher atomic value was enlarged. It therefore becomes possible to prepare filters bearing analogous absorption performances over broad compositional ranges, although it is especially desirable, from the standpoint of preparing a filter bearing a favorable chemical endurance & virtually unaccompanied by manufacturing difficulties, to use a fluorophosphate glass wherein the ratios of P_2O_5 & the respective metal fluorides are confined to the following ranges:

	Wt%
P_2O_5	10 ~ 30
AlF_3	8 ~ 30
$BaF_2 + SrF_2 + CaF_2 + MgF_2$	50 ~ 70
BaF_2	0 ~ 40
SrF_2	0 ~ 40
CaF_2	0 ~ 30
MgF_2	0 ~ 20
LiF	0 ~ 20

$LaF_3 + YF_3$ 0 ~ 8

(it is also possible to substitute no more than 50% of the total metal fluoride internalization ratio with metal oxides).

It is also possible, depending on applications, to modify the transmissivity curve by adding, to the aforementioned fluorophosphate base glass, small quantities of transition metal oxides instantiated, in terms of wt%, by no more than 0.6% of Cr_2O_3, no more than 0.01% of Fe_2O_3, no more than 0.01% of Co_2O_3, no more than 0.01% of NiO, no more than 0.01% of V_2O_5, no more than 0.005% of MnO_2, no more than 0.005% of CuO, and no more than 0.5% of Eu_2O_3. Oxides bearing extremely intense absorptions within the ultraviolet region such as PbO, TiO_2, Nb_2O_5, WO_3, etc., however, may not be included.

The transmissivity or absorbance gauge of a spectrophotometer is calibrated according to the following procedures by using the optical glass filter of the present invention for calibrating the transmissivity or absorbance within the ultraviolet region obtained by adding CeO_2 to the aforementioned fluorophosphate base glass. In other words, 0% & 100% transmissivity adjustments are rendered upon the stabilization of the spectrophotometer after its power source has been turned ON, and subsequently, the measurement wavelength & band path are designated. On this occasion, the designated measurement wavelength & band path displayed on a calibration optical glass filter are used. Air is provided as a control luminous flux, and the calibration optical glass filter is mounted on the sample luminous flux side. Incidentally, it is necessary to calibrate the wavelength gauge in advance on an occasion for calibrating the transmissivity or absorbance gauge. The wavelength gauge is hereby calibrated by using the line wavelength of a heavy hydrogen lamp or low-pressure quartz mercury lamp together with a wavelength calibration filter. In the case of a spectrophotometer endowed with a temperature control mechanism, the temperature is maintained at 23.5°C, and the transmissivity is measured after the verification of the achievement of a constant temperature. The spectrophotometer is calibrated by repeating the transmissivity measurements of the mounted calibration optical glass filter three times. The average of the obtained values is

calculated and defined as the measurement value, and after its differential from the value of the calibration optical glass filter (the value of which is to be assessed by an official organization on a later date) has been calculated, it is defined as the built-in differential of said spectrophotometer. Moreover, in a case where the transmissivity is measured, it is desirable to use two or more types of calibration optical glass filters with mutually different transmissivities. In a case where the transmissivity of an actual sample is measured, furthermore, it is possible to calculate an accurate transmissivity by subtracting this built-in differential of the spectrophotometer from an actual measurement value.

It is also possible to calibrate the absorbance gauge of a high-absorbance region by orchestrating the so-called "multi-filter format," whereby two or more filters are laminated.

(Application examples)

In the following, the present invention will be explained in further detail, although the present invention is not limited to these application examples.

Application Example 1 /4

(1): Preparations of optical glass filters

Such feed materials as o-phosphoric acid (used as an aqueous solution), aluminum hydroxide, aluminum fluoride, barium fluoride, strontium fluoride, calcium fluoride, magnesium fluoride, lithium carbonate, lithium fluoride, etc. each bearing high purities permissible as raw ingredients for manufacturing glasses were used {incidentally, the use, as a feed material, of a composite oxide (e.g., aluminum phosphate, etc.) is not prohibited}. After a mixture of the aforementioned feed materials had been filled into a platimum melting pot, it was melted, agitated, homogenized, & defoamed at 800 ~ 1,000°C, and after the obtained molten batch had been cast into a mold preheated at an appropriate temperature, it was gradually cooled, as a result of which four

types of glass filters, namely Nos. 1 ~ 4, bearing the compositions of the respective components shown in Table I were prepared.

Table I

Sample No.	1	2	3	4	Commercial ND glass filter

P_2O_5	11.0	23.0	27.0	32.2	
Al_2O_3	3.0		5.0	2.4	2.0
AlF_3	28.0	20.0	10.0	7.5	
BaF_2	12.0	25.0	15.0		
SrF_2	20.0	15.0	15.0	12.2	
CaF_2	16.0	12.0	11.0	1.0	
MgF_2	7.0	5.0	6.0	0.4	
Li_2O			5.0		
LiF			6.0		
NaF	3.0				
BaO				40.0	
MgO				4.3	
CeO_2	0.008	0.01	0.1	0.1	
SiO_2					62.0
B_2O_3					19.0
K_2O					10.0
Na_2O					4.0
ZnO					5.0
Cr_2O_3	0.15				
Fe_3O_4					3.0
Co_2O_3	0.005				0.04

(2): Measurements of spectral transmissivities of the obtained optical glass filters

Spectral transmissivity curves pertaining, at a thickness of 2 mm, to the respective glass filter Nos. 1 ~ 4 obtained in the present application example and a commercial ND glass filter (the composition of which is shown in Table I) are shown in Figure 1.

It can be judged from Figure 1 that, in contradistinction with the commercial ND glass filter, which yields a zero transmissivity in the vicinity of 350 nm and which does not transmit beams at shorter wavelengths, the respective glass filter Nos. 1 ~ 4 of the present application example are suitable for the calibration of the transmissivity or absorbance within the ultraviolet region, for they each bear relatively moderate transmissivity curves within a range of 200 ~ 300 nm.

Application Example 2

(1): Preparations of optical glass filters

Four types of optical glass filters, namely Nos. 5 ~ 8, were prepared by using various feed material compounds according to procedures otherwise similar to those in (1) of Application Example 1. Incidentally, the respective glass filter compositions of Nos. 5 ~ 8 were provided by changing the CeO_2 internalization ratio of the aforementioned glass filter of No. 2, namely 0.01%, to 0.008% (No. 5), 0.016% (No. 6), 0.029% (No. 7), or 0.053% (No 8), whereas the respective quantitative ratios of the other glass components, namely P_2O_5, AlF_3, BaF_2, SrF_2, CaF_2, and MgF_2, are identical to their counterparts of the glass filter of No. 2.

(2): Performance tests on obtained optical glass filters

Requirements to be met by calibration filters include the stability of transmissivity value, low temperature coefficient, resistance against ultraviolet exposure degradation, etc., and accordingly, the following tests were conducted.

①: Transmissivity stability test

Each of optical glass filter Nos. 5 ~ 8 cut into a size of 10 ×10 × 35 mm was supported on a cuvette-type retention frame, and after the obtained module had been installed within the sample cell of a calibration spectrophotometer, transmissivities at various wavelengths were repeatedly measured, and the repetition precisions of measurement values were investigated.

The obtained results are shown in Table II.

Table II (Part 1) /5

Sample \ measurement wavelength	207 nm	211 nm	222 nm	229 nm
No. 5	60.131±0.049	60.690±0.042	57.220±0.068	58.696±0.060
No. 6	52.486±0.042	53.287±0.037	46.669±0.062	48.356±0.040
No. 7	27.617±0.060	28.382±0.066	26.147±0.070	31.040±0.075
No. 8	25.986±0.0283	27.104±0.036	20.068±0.058	21.833±0.054

Table II (Part 2)

Sample \ measurement wavelength	235 nm	237 nm	263 nm	280 nm

No. 5	56.891±0.049	55.088±0.051	55.366±0.080	60.132±0.100
No. 6	44.857±0.032	37.592±0.061	36.991±0.075	42.004±0.084
No. 7	27.548±0.024	19.566±0.019	18.804±0.025	23.318±0.051
No. 8	17.851±0.038	9.739±0.042	8.993±0.044	11.713±0.061

The repetition precisions of transmissivity were somewhat inferior a case where the measured transmissivity of the filter was high or where the measurement wavelength was long, although in a case where the magnitudes of these variations are expressed in terms of ratios with respect to the transmissivity average measurement value (variation coefficients), the maximal value is only 0.17%, whereas the average is 0.1% or below.

It was confirmed, in contrast, that the maximal transmissivity variation of a case where a potassium bichromate solution was repeatedly prepared was as high as 0.33% in terms of the transmissivity differential attributed to preparation at the respective peak concentrations on three preparation occasions, whereas since this magnitude is equivalent to nearly 1% with respect to the measured transmissivity, the superiority of the optical glass filter of the present invention is obvious in terms of the stability of measurement values.

②: Temperature test

Effects of temperature on transmissivity were investigated by measuring the respective transmissivities of optical glass filter No. 7 at 10°C & 50°C. The obtained results are shown in Figure 2, according to which a wavelength unaffected by temperature, namely a so-called "isosbestic point," exists within the spectrum in terms of the effects of temperature on the ultraviolet filter transmissivity, and a peculiar temperature profile whereby the transmissivity increased in accordance with a temperature gain on the longer wavelength side of this threshold and whereby the transmissivity conversely decreased on the shorter wavelength side of the same was observed.

More precise measurements have revealed that this temperature-specific isosbestic point (P) exists in the vicinity of 250 nm and is independent of the types of filters. The magnitude of the transmissivity variation attributed to temperature, however, is only approximately ±0.01%/°C or so at the most, and therefore, it has been confirmed that the effects of temperature on measurement values are negligible so long as temperature variations are minimized on measurement occasions in the course of ordinary measurement tasks.

③: Ultraviolet exposure degradation test

A test was conducted in compliance with Japan Optical Glass Industrial Society Standards JOGIS-04, as a result of which no transmissivity variations were acknowledged over the entire region of 200 ~ 400 nm with regard to every sample.

It was judged, based on the foregoing test results, that the present glass filter Nos. 5 ~ 8 of Application Example 2 are suitable as filters for calibrating the transmissivity or absorbance within the ultraviolet region. /6

Incidentally, in a case where the respective glass filter Nos. 1 ~ 4 obtained in Application Example 1 were subjected to the ①: Transmissivity stability test, ②: Temperature test, & ③: Ultraviolet exposure degradation test according to similar procedures, results similar to those on glass filter Nos. 5 ~ 8 of Application Example 2 were obtained.

(Effects of the invention)

As the foregoing detailed explanations have demonstrated, the filter of the present invention not only bears a moderate transmissivity curve over a broad range of 200 ~ 300 nm corresponding to the ultraviolet region but also bears the following advantages:

(1): Favorable measurement value accuracy & repetition precision;

(2): The applicability, due to minimal effects of temperature, of the isosbestic point to wavelength calibration;

(3): Use of an inexpensively accessible glass, which also affords a favorable handling friendliness & simplified maintenance & management;

Etc., and thus, it can be used favorably as a filter for calibrating the transmissivity or absorbance within the ultraviolet region.

4. Brief explanation of the figures

Figure 1 is a diagram which shows the respective transmissivity curves of glass filter Nos. 1 ~ 4 of the present invention and a commercial ND glass filter, whereas Figure 2 is a diagram which shows the temperature-specific variation of the transmissivity curve of glass filter No. 7 of the present invention.

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Mechanical & Electronic Inspection & Certification Society, government foundation

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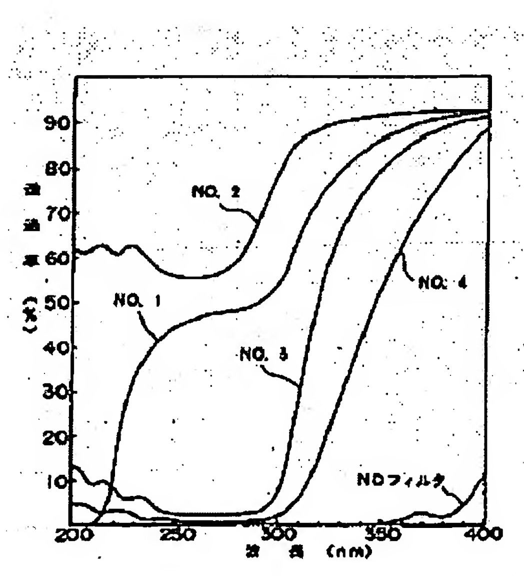
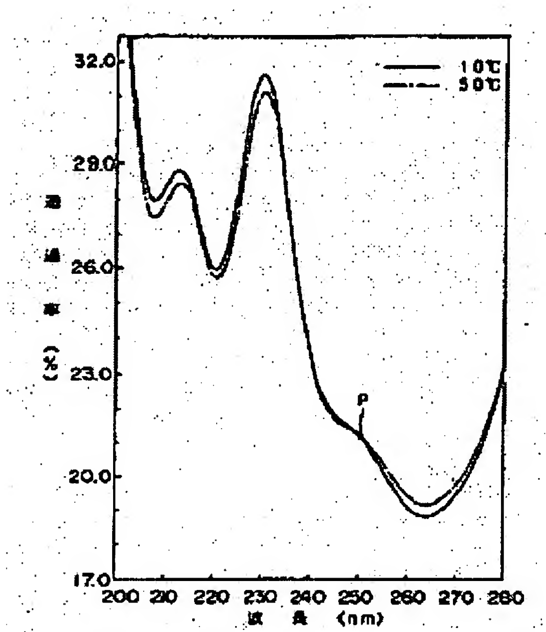
Figure 1



[(1): Transmissivity (%); (2): Wavelength (nm)]

Figure 2



[(1): Transmissivity (%); (2): Wavelength (nm)]